Project ID: ACS119

Development and Optimization of a Multi-Functional SCR-DPF Aftertreatment System for Heavy-Duty NO_X and Soot Emission Reduction

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Pacific Northwest National Laboratory

DOE Annual Merit Review
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OVERVIEW

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Timeline

- 4-yr CRADA
  - Start date – July 2016
  - End date – June 2020
- 16.7% complete

Barriers

- **B. Lack of cost-effective emission control** for meeting EPA standards for NOx & PM
- **E. Durability** of the emission control system: 435,000 miles
- **G. Cost** of emission control devices … for heavy truck engines in particular

Budget

- Contract value – $2.7M
  - $1.35M DOE Share
  - $1.35M PACCAR Share
- Funding received
  - FY16 – $200K
  - FY17 – $355K

Partners

- CRADA partner – PACCAR Inc
- PACCAR Inc – multiple contracts in place in support of advanced aftertreatment development and engineering

RELEVANCE
Multi-Functional Aftertreatment

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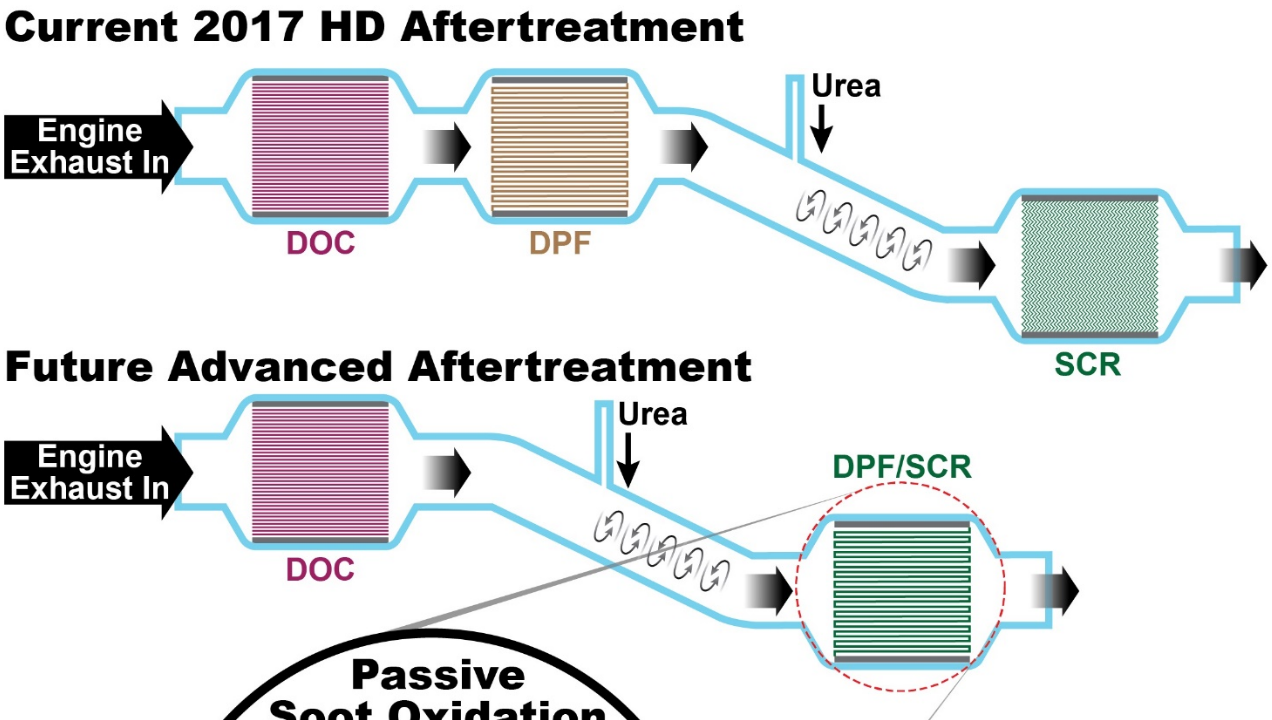
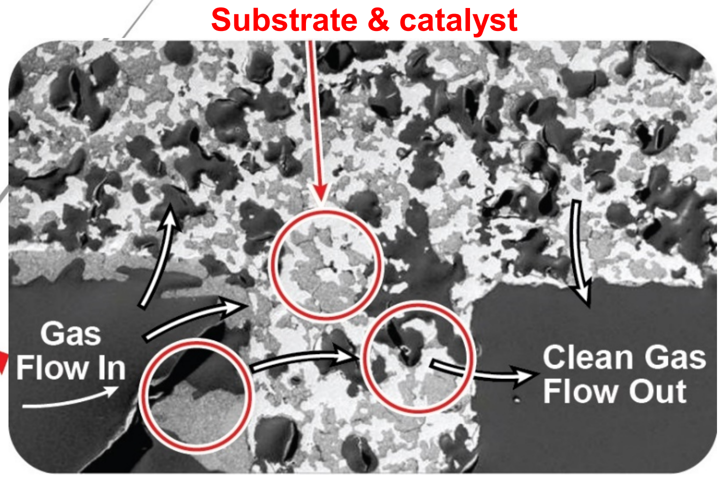


SCR-on-DPF

Key:
Enabling passive soot oxidation



Soot trapped upstream

Molecular diffusion to washcoat

RELEVANCE
SCR-on-DPF

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- Highly promising strategy for after-treatment integration
  - Reduced thermal mass & faster warm-up – reduced cold start emissions
  - Improved aftertreatment performance & increased flexibility

- LIGHT DUTY – challenges

  1. **Sufficient SCR performance**
     - Ultra-high porosity filter development (Corning, NGK)

       Enables more SCR catalyst at acceptable engine back pressure
     - Advanced filter coating, imaging techniques (e.g., PNNL micro-Xray-CT)

       Optimized catalyst placement and usage in the filter wall
  2. **SCR catalyst durability**
     - ... to withstand ***active*** soot oxidation management

       Cu/SSZ-13 – more thermally durable, a key enabler

- *Currently being deployed for light-duty application*

http://www.catalysts.basf.com/p02/USWeb-Internet/en_GB/content/microsites/catalysts/prods-inds/mobile-emissions/scr-filter

http://papers.sae.org/2016-01-0915/

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- HEAVY DUTY – challenges
  1. Sufficient SCR performance
  2. SCR catalyst durability
  3. **Passive soot oxidation performance (via NO_2)**
     - Economically attractive to manage soot passively for heavy duty
     - With incorporation of SCR phase, *competition for NO_2*

fast-SCR $2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$

Dominates NO_2 consumption

versus

Significantly compromises soot oxidation

passive soot oxidation $C\ (soot) + 2NO_2 \rightarrow CO_2 + 2NO$

SOLUTION

- Modify the SCR catalyst to generate NO_2 in situ

APPROACH
Summary

FOCUS OF WORK

- Development of ***a novel SCR active phase*** for the SCRF system that exhibits sufficient *passive soot oxidation* and *NO_X reduction efficiency* at acceptable ΔP to be attractive for HD diesel application
- **How?**
  - An SCO-SCR binary catalyst system – incorporation of a selective catalyst oxidation (SCO) metal oxide phase with the SCR catalyst.
  - The binary catalyst will yield greater availability of NO_2 in the system ***without*** sacrificing necessary NO_x reduction performance or durability
- PNNL and PACCAR are pursuing …
  - Advancement of the SCO-SCR binary catalyst that is achievable in the time frame proposed
  - … to make its integration with DPF a viable candidate for combined NO_x and PM aftertreatment for heavy-duty

APPROACH

Timeline

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Phase 1	Phase 2	Phase 3	Phase 4
■ Feasibility/approach ■ SCO identification	■ SCO-SCR development ■ SCRF optimization	■ 2-liter scalability	■ Full-scale scalability
12 Months	24 Months	36 Months	48 Months

DEVELOPMENT of SCO-SCR BINARY CATALYST

- Sample screening
- SCO phase screening
- SCO-SCR binary catalyst fundamental and aging studies
- SCO-SCR binary catalyst optimization

CATALYST INTEGRATION w/DPF

- Coating procedure
- Catalyst loading/distribution
- Substrate/porosity

SCR-on-DPF MODEL DEVELOPMENT

- Model platform development
- Reaction matrix, parameter optimization, modeling aging behavior
- Device-level model development

2-L SCR-on-DPF SCALING/TESTING

FULL-SCALE SCR-on-DPF

APPROACH
Milestones

Date*	Milestone and Go/No-Go Decisions	Status
November 2016	Milestone: 1st group of PACCAR SCO/SCR binary-phase catalyst samples delivered to PNNL for testing	Complete
February 2017	Milestone: Large-batch Cu/SSZ-13 SCR phase prepared and ready for SCO phase development	In-progress
May 2017	Milestone: Structure of integrated SCR-DPF single-wall model complete	In-progress
August 2017	Milestone: 1st group of SCO/SCR binary-phase catalysts with candidate SCO phases (preferably <3) ready for fundamental study	On-track
November 2017	Milestone: 1st group of optimized SCRF samples with candidate SCO/SCR binary catalyst ready for detailed testing	On-track
February 2018	Go/No-Go decision: Identify candidate SCO/SCR binary phase catalyst with improved soot oxidation performance with competing SCR	On-track

* As of 04/10/2017

TECHNICAL ACCOMPLISHMENTS
Model System Parameter Screening

- Selective parameter screening with ZSM-5 model system
  - Focused on ZrO_2–based SCO phase, to evaluate the effect of …
    - SCO phase on Cu/ZSM-5 performance
    - Binary catalyst mass ratio (SCO to SCR)
    - Binary catalyst loading
    - Varying catalyst preparation procedures (i.e., different ‘lots’)
    - Catalyst loading symmetry
    - ZrO_2 source
  - PACCAR
    - Sample acquisition/preparation
  - PNNL
    - Performance & durability assessment
- Detailed interrogation of SCR and contributing reaction performance
  - Multi-step protocol testing
- Soot loading & passive soot oxidation study

TECHNICAL ACCOMPLISHMENTS
Impact of SCO-phase on NO_2 balance

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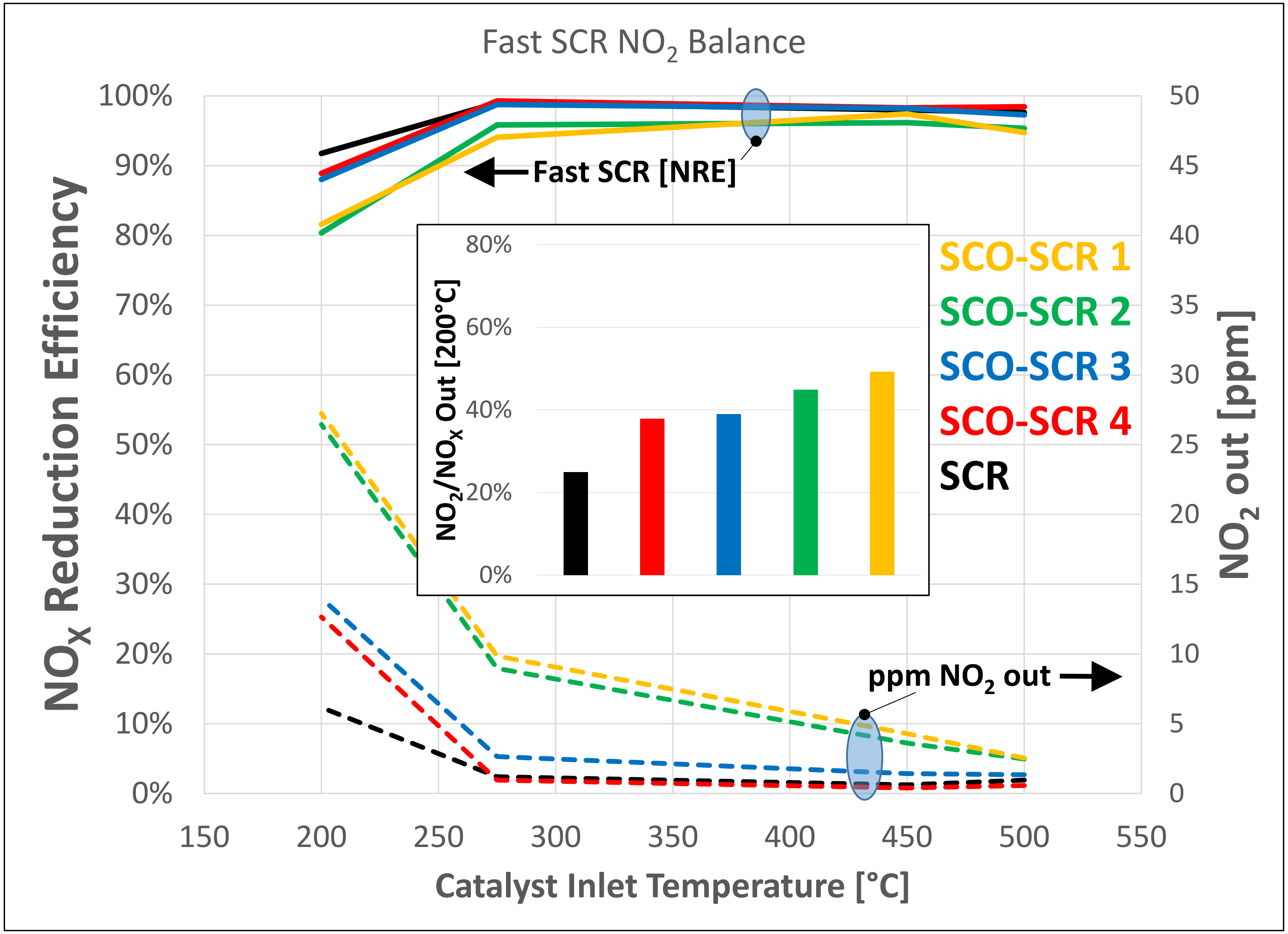
- NO_2



NO_2 balance
- total ppm
- NO_2/NO_x

… **IS** impacted by SCO-phase contribution

TECHNICAL ACCOMPLISHMENTS
Impact of SCO phase on NRE

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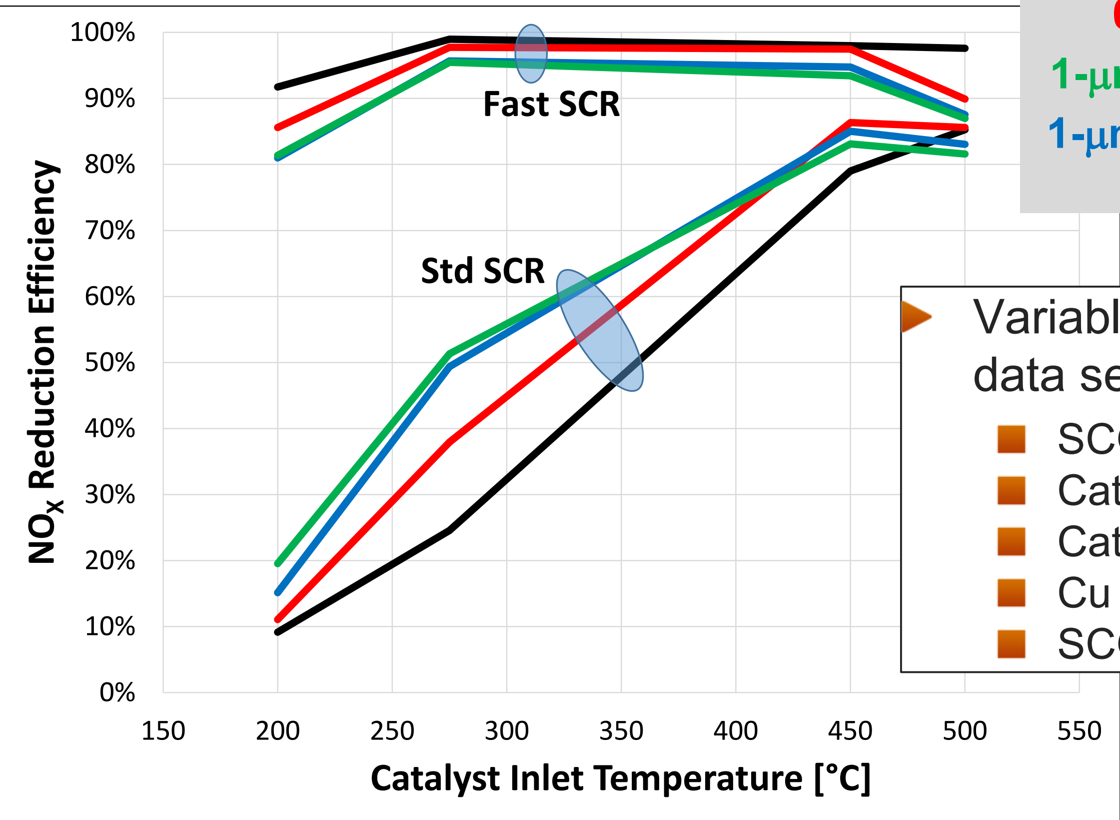
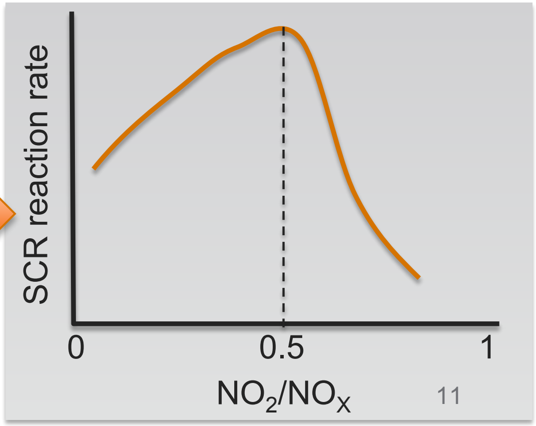
No SCO phase
0.1-µm colloidal ZrO_2
1-µm ZrO_2 (600°C decomp.)
1-µm ZrO_2 surface modified w/ Nb_2O_5



- Variables involved in this data set include …
  - SCO-phase chemistry
  - Catalyst ratio
  - Catalyst loading
  - Cu loading
  - SCO-phase particle size

- We <u>ARE</u> seeing the expected impact of increased NO oxidation on SCR performance (standard & fast)



TECHNICAL ACCOMPLISHMENTS
SCO/SCR system optimization

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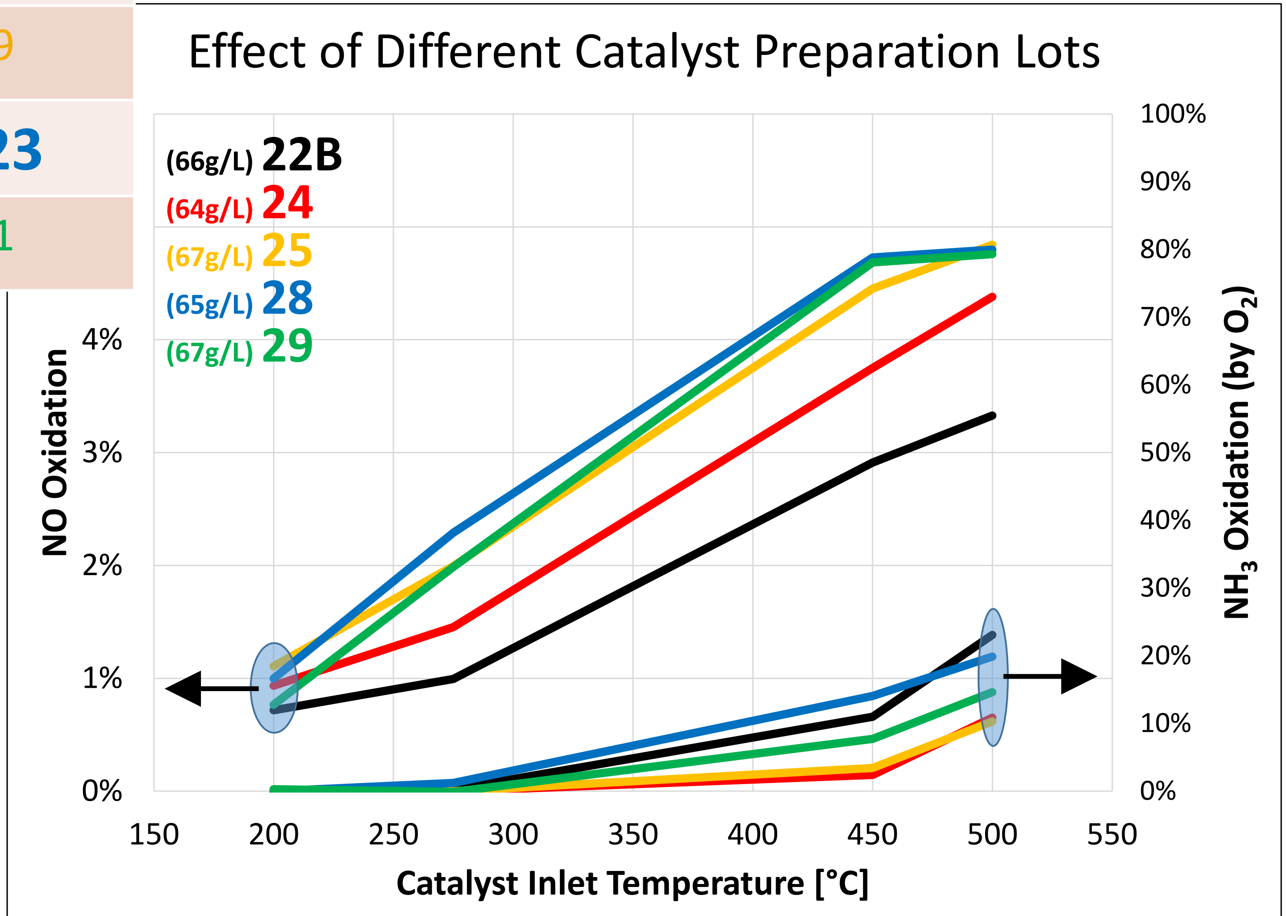
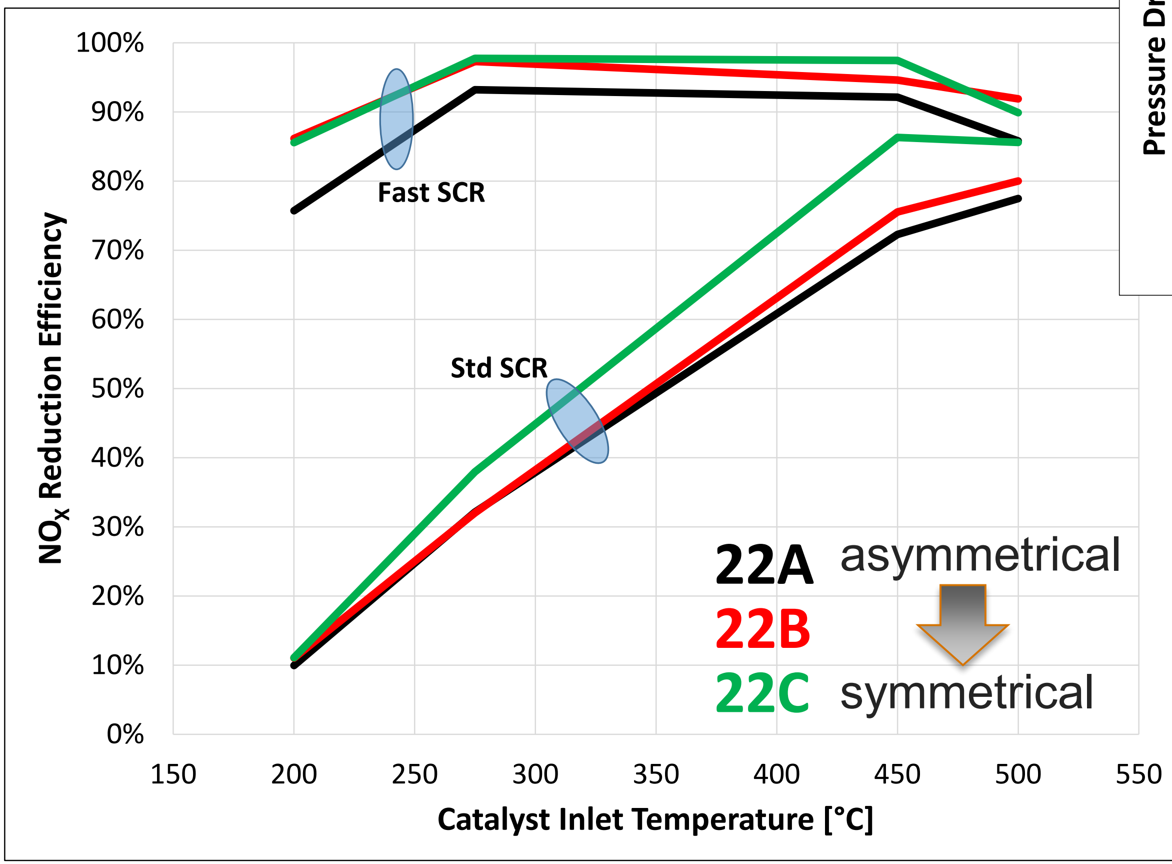
Sample	Cu (wt%)
22B	0.84
24	0.30
25	0.19
28	0.23
29	0.21

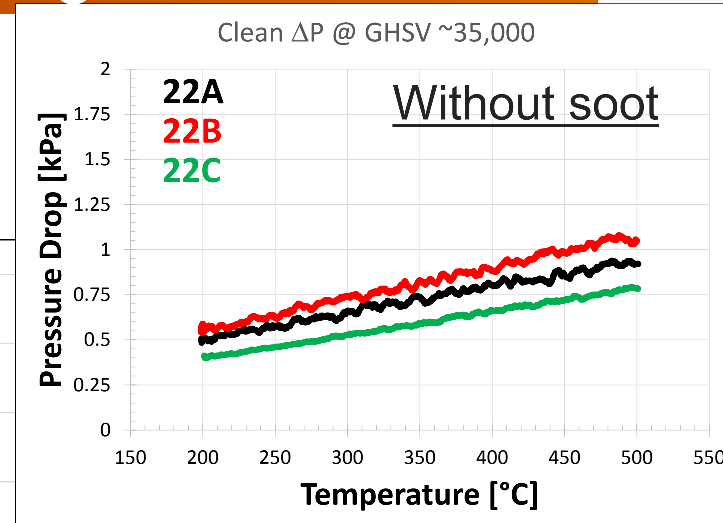
- NO oxidation also governed by SCR catalyst (e.g., Cu exchange level)
- Thus, optimization WILL necessarily consider both SCO and SCR phases



TECHNICAL ACCOMPLISHMENTS
Multi-functional device engineering

- Symmetrical versus asymmetrical catalyst loading





- Improved activity with superior dispersion
- … at lower pressure drop.

For multi-functional devices, device engineering (*led by PACCAR*) is a critical component to success

TECHNICAL ACCOMPLISHMENTS
Impact(s) of soot/catalyst on each other

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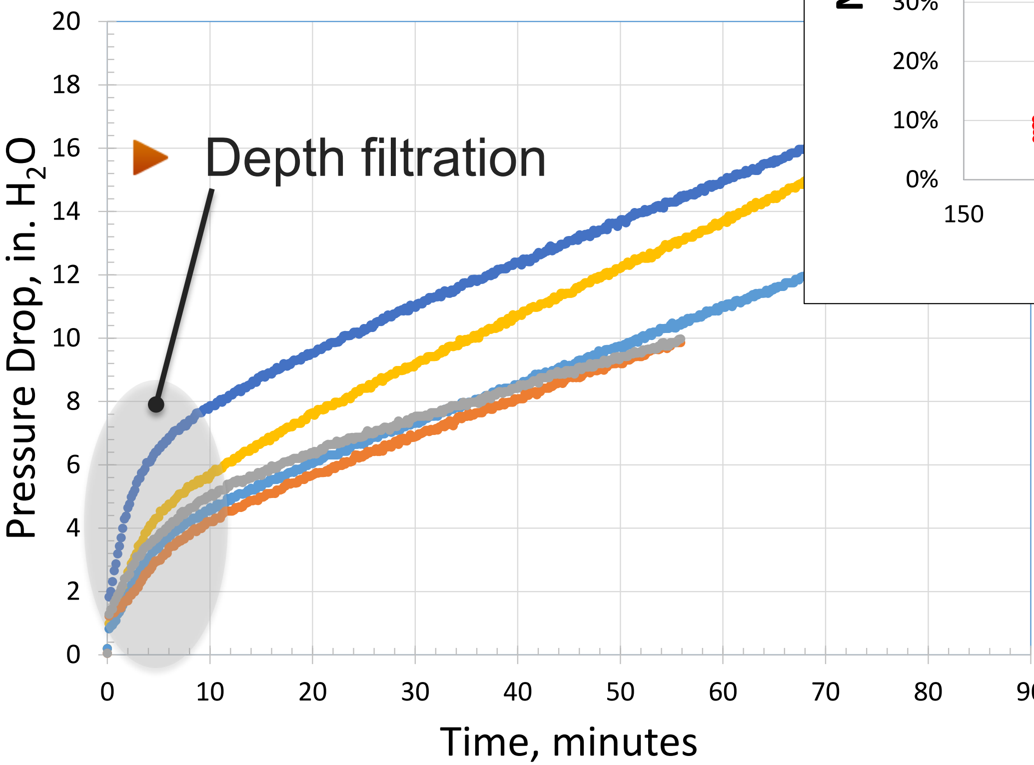
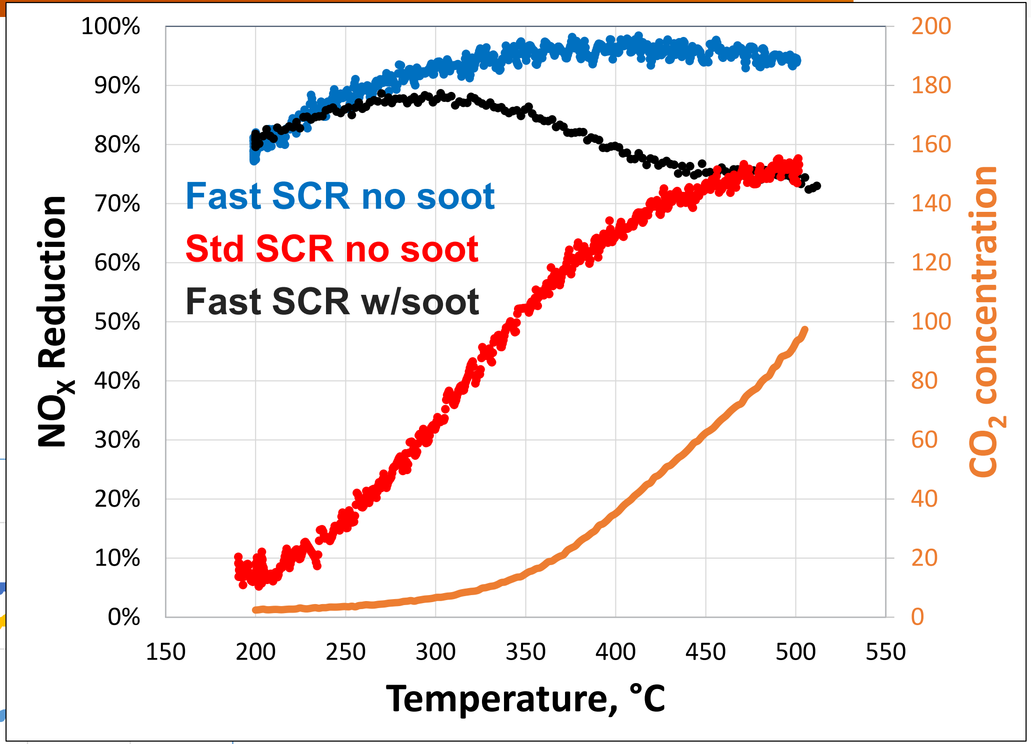
Soot ⇔ SCR

SCR catalyst mainly impacts depth filtration of soot



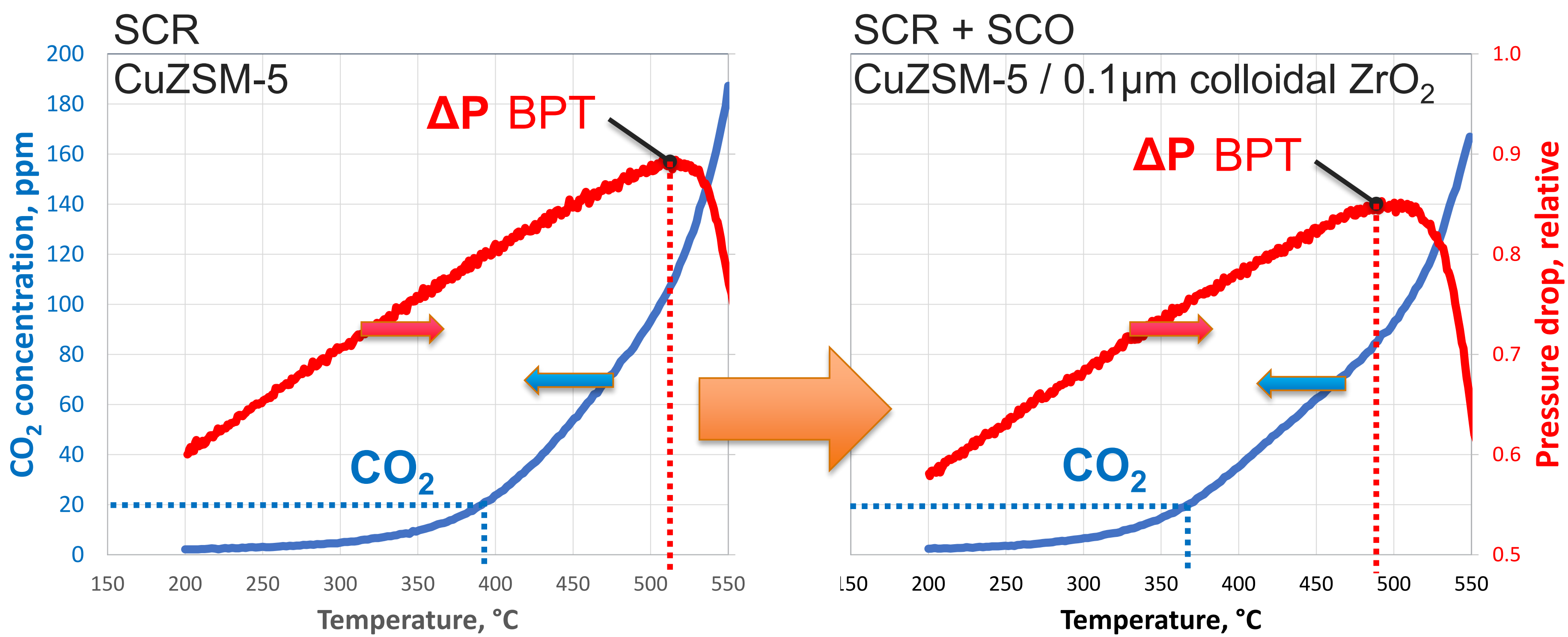


Primary impact of soot on SCR function is on NO_x make-up

<u>Elucidating prior work</u>

TECHNICAL ACCOMPLISHMENTS
SCO phase impacting soot oxidation

- Passive soot oxidation (PSO)



PSO metric	SCR	SCR + SCO
20ppm CO_2 production	395°C	365°C
Balance Point Temperature	515°C	490°C

SCO phase **IS** impacting passive soot oxidation light-off

REVIEWER COMMENTS

- First year of program, no comments to address.

Collaboration & Coordination

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- Fundamental catalysis discovery
- Active site characterization & optimization
- Performance & durability
- Modeling

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- SCO phase discovery
- SCRF washcoat development
- SCR phase development
- DPF optimization

DPF Substrate Suppliers
- Cordierite
- SiC

SCR Catalyst Development
- Mesoporous Cu/SSZ-13

Catalyst Suppliers

Prototype Canners

Remaining Challenges & Barriers

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FY17/18

- Identification of optimum SCO metal oxide phase, that when integrated with the SCR phase (Cu/SSZ-13), …
  - **… enables passive soot oxidation capacity for HD diesel …**
    - Identification of optimum SCO-phase metal oxide chemistry (e.g., ZrO_2, Zr-based solid solutions) to generate NO_2 at the SCR catalyst surface
    - Methods of efficiently screening SCO candidates (i.e., catalyst discovery) that accurately predict/determine passive soot oxidation impact
  - **… while exhibiting necessary SCR performance.**
    - Identification of SCO-phase metal-oxide chemistry that balances activity for NO_2-make with subsequent effect on (i) SCR durability, and (ii) parasitic NH_3 oxidation at elevated temperature
    - Optimizing method of integration of the SCO-phase with the SCR catalyst that achieves the necessary activity (NO_2) and durability (SCR)
    - Understanding the impact of the SCO-phase on performance & aging-behavior of active Cu-centers

Future Work

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FY17/18 Any proposed future work is subject to change based on funding levels

- Complete ZSM-5 model system study for metal oxide screening
  - Needs to be quick!
  - High-level screening for candidate identification
- Clearly show feasibility on Cu/SSZ-13
  - Surface nitrate formation (transmission IR, TPD)
  - SCR reaction performance
- Directly correlate to soot oxidation impact, and use correlation to guide SCO-phase evolution
  - Iterate surface science and active-phase (i.e., powder) study to core for evaluating passive soot oxidation impact
- Develop strategy for understanding SCO-phase impact on SCR behavior & durability
  - Active Cu centers (TPR, EPR), understanding impact of aging and Cu transition: $Cu(OH)^{1+}$ to Cu^{2+} to Cu_xO_y
  - SSZ-13: NMR

SUMMARY

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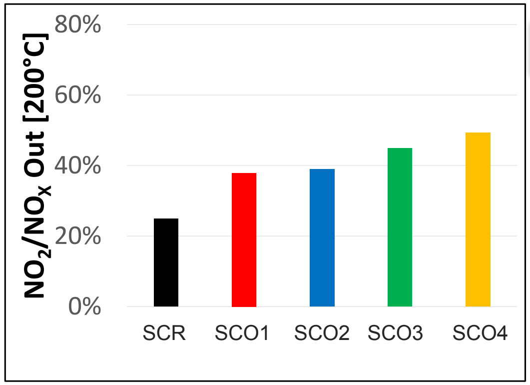
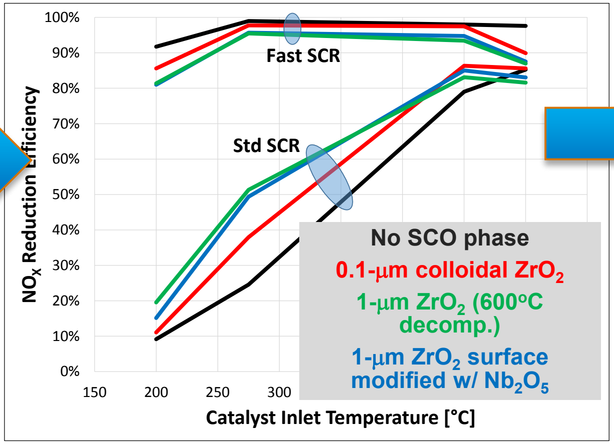
Aftertreatment ***effectiveness, durability, cost***

SCO-SCR binary catalyst development





Sample	Cu (wt%)
22B	0.84
24	0.30
25	0.19
28	0.23
29	0.21

22A asymmetrical
22B
22C symmetrical

Soot SCR

PSO metric	SCR	SCR + SCO
20ppm CO_2 production	395°C	365°C
Balance Point Temperature	515°C	490°C

Technical Back-Up Slides

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- Technical Back-Up Slides

Technical Back-Up Slides
SCRF – findings from prior CRADA

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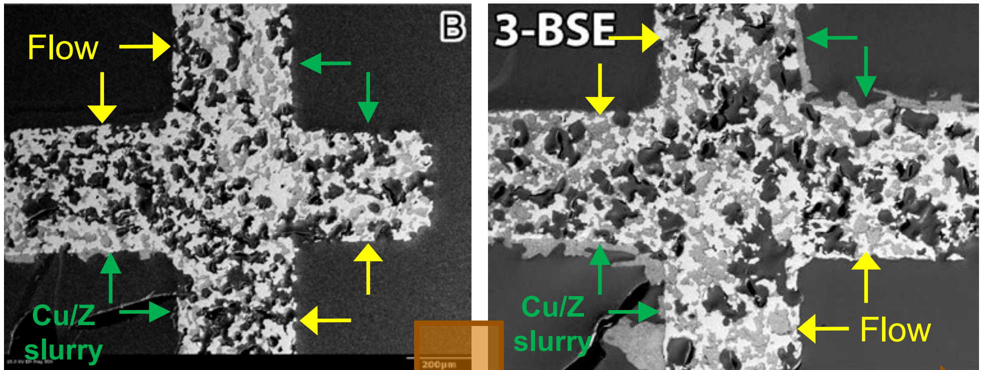
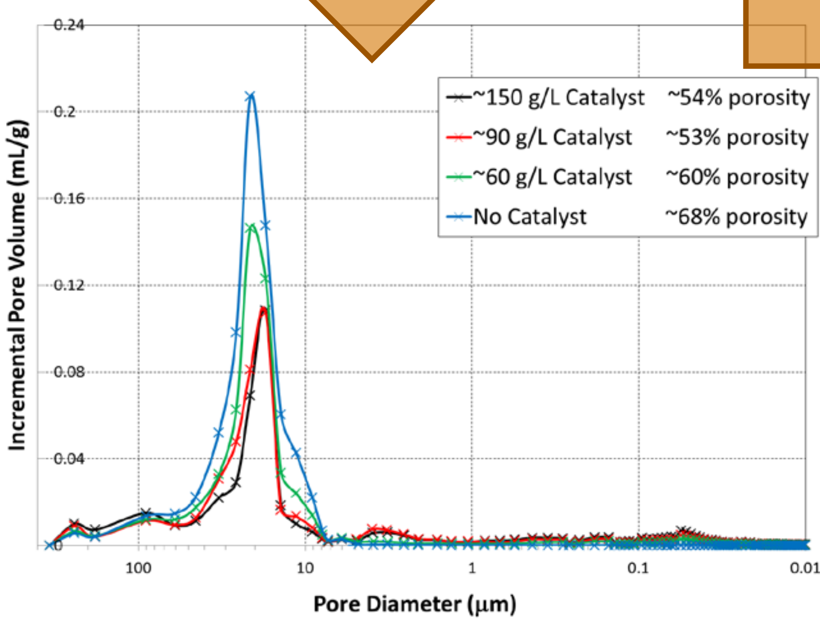
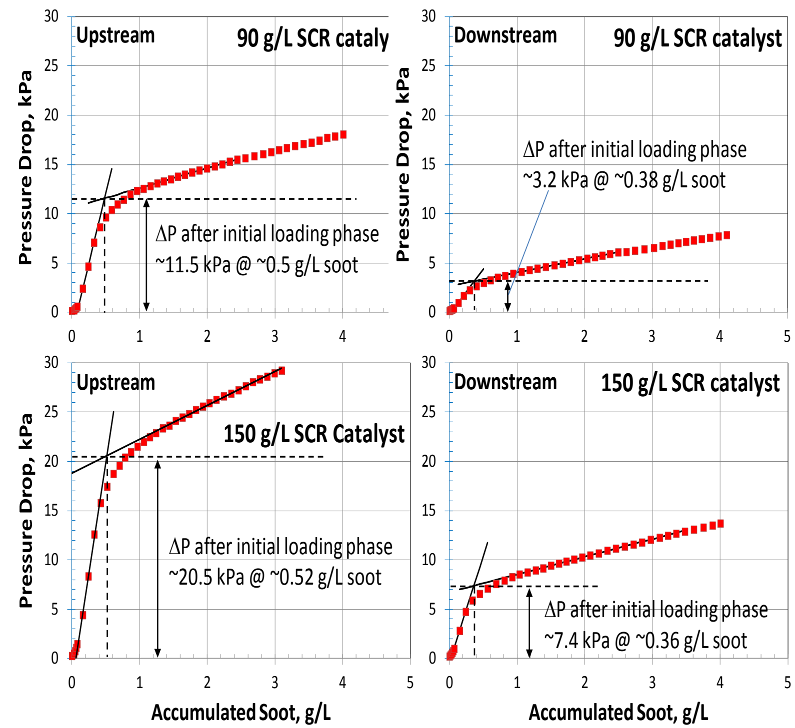
- The SCRF washcoat







Technical Back-Up Slides

SCR reaction network (simplified)

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$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

$$NO + \tfrac{1}{2} O_2 \rightleftharpoons NO_2$$

$$\mathbf{2NH_3 + 2NO + \tfrac{1}{2}O_2 \rightarrow 2N_2 + 3H_2O}$$

- **Standard SCR reaction ($NO_2/NO_X = 0$)**

$$\mathbf{2NH_3 + 2NO + 2NO_2 \rightarrow 2N_2 + 3H_2O}$$

- **Fast SCR reaction ($NO_2/NO_X = 0.5$)**

$$\mathbf{8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O}$$

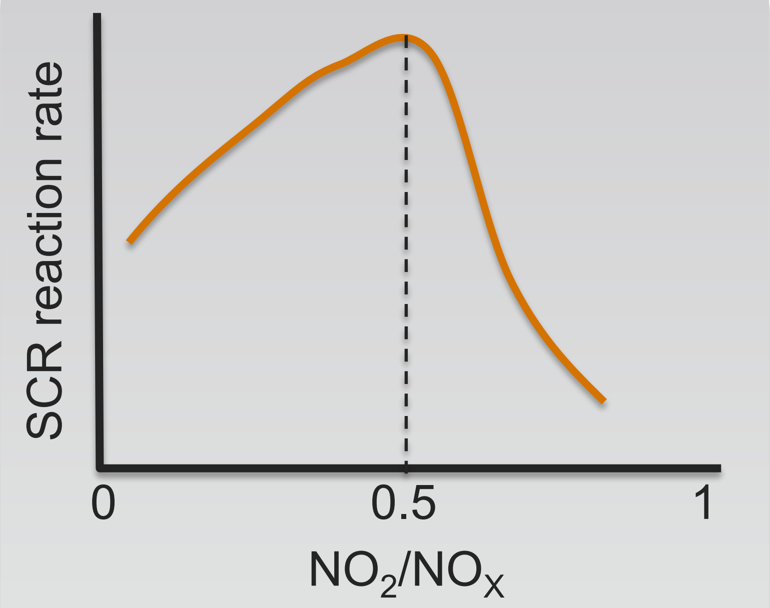
- **NO_2-only SCR reaction ($NO_2/NO_X = 1$)**

$$2NO_2 + 2NH_3 \rightarrow N_2 + H_2O + NH_4NO_3$$

$$NH_4NO_3 \rightleftharpoons NH_3 + HNO_3$$

$$2NO_2 + H_2O \rightleftharpoons HONO + HNO_3$$

$$NH_3 + HNO_3 \rightarrow N_2O + 2H_2O$$



Technical Back-Up Slides

8 Step SCR Protocol

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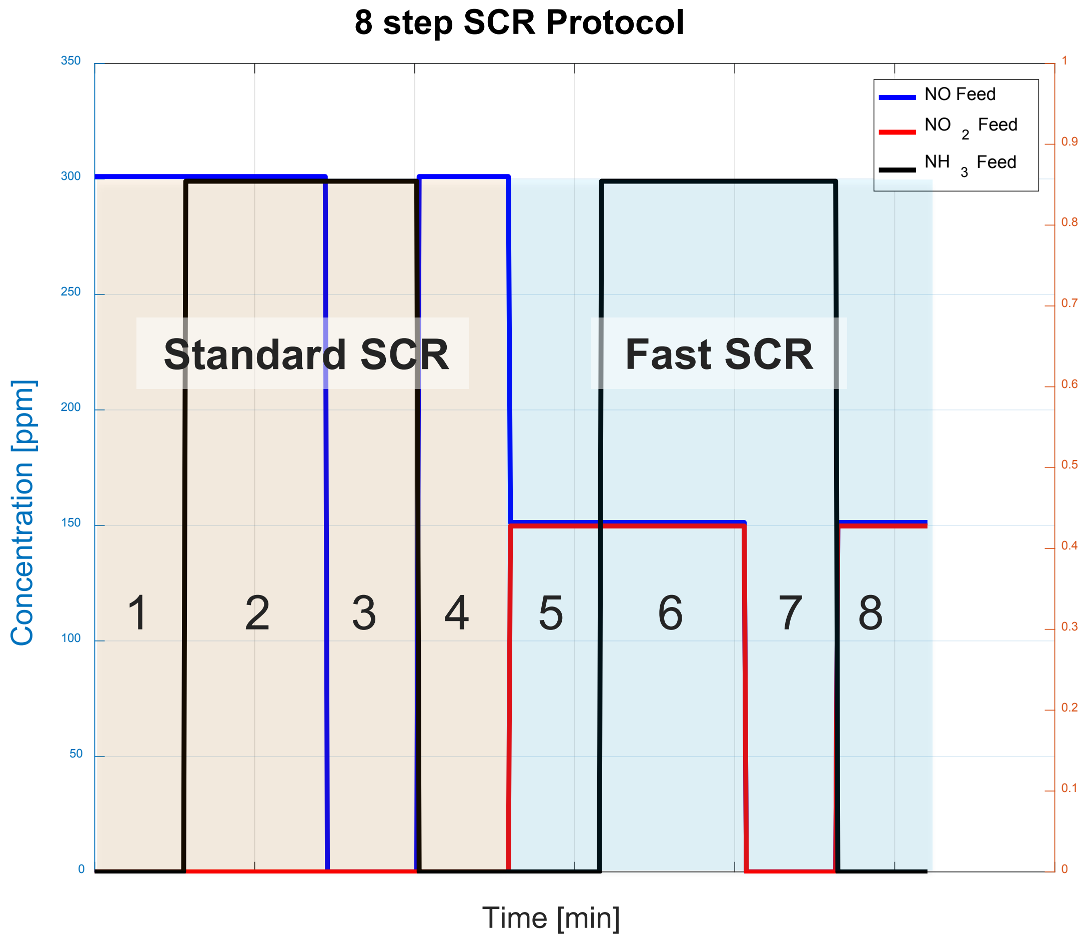
- 10% O_2, 8% CO_2, 7% H_2O, 300 ppm NO_X, 300 ppm NH_3
- Pre-treatment – 60 minutes @ 600°C
- Protocol executed at 500°C, 450°C, 275°C, 200°C



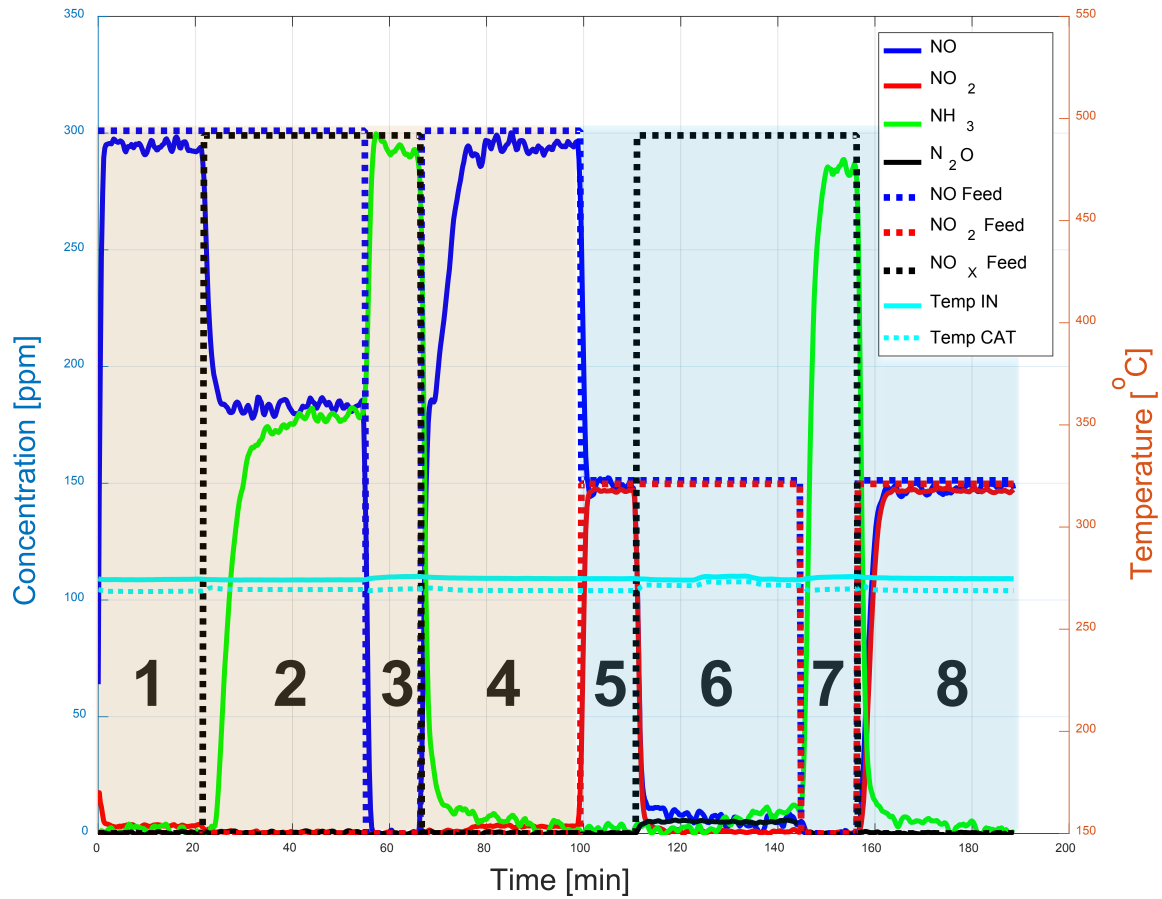
	Concentration [ppm]		
Step #	NO	NO_2	NH_3
1	300	0	0
2	300	0	300
3	0	0	300
4	300	0	0
5	150	150	0
6	150	150	300
7	0	0	300
8	150	150	0

Technical Back-Up Slides
Information Gathered

- Steps 1 & 5
  - NO oxidation (to NO_2)
  - NO_X storage
- Steps 2 & 6
  - SCR performance
  - NH_3 slip
  - Parasitic NH_3 oxidation
  - N_2O selectivity
  - NO_2/NO_X in effluent
  - NH_3 SCR storage
- Steps 3 & 7
  - NH_3 oxidation (by O_2)
  - Vacant NH_3 storage
- Steps 4 & 8
  - Total NH_3 storage

Example graphical data

Protocol Data at 275°C: Sample 22C



Technical Back-Up Slides
Example tabular data

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				Temperature [°C]			
		SCR reaction		500	450	275	200
Step 1	SS	standard	NO oxidation	4.7%	4.4%	2.1%	0.9%
	D	standard	NO_X storage	19.5	17.8	31.2	25.4
Step 2	**SS**	**standard**	**NO_X conversion**	**85.3%**	**79.0%**	**24.6%**	**9.1%**
	SS	standard	NH_3 slip	10.4%	13.0%	72.3%	92.8%
	SS	standard	Parasitic NH_3 oxidation	4.3%	8.0%	3.1%	0%
	SS	standard	N_2O selectivity	0.4%	0.5%	0.3%	0%
	SS	standard	NO_2/NO_X effluent	2.2%	1.5%	0.2%	0.1%
	D	standard	NH_3 storage (SCR)	74.6	56.5	623.5	891.4
Step 3	SS	standard	NH_3 oxidation (by O_2)	18.5%	11.4%	1.1%	0%
	D	standard	NH_3 storage (vacant)	161.9	161.8	58.6	11.4
Step 4	D	standard	NH_3 storage (total)	213.7	268.3	702.8	737.9
Step 5	SS	fast	NO oxidation	0%	3.6%	7.2%	5.9%
	D	fast	NO_X storage	25.3	26.1	17.2	17.3
Step 6	**SS**	**fast**	**NO_X conversion**	**97.6%**	**98.0%**	**99.0%**	**91.7%**
	SS	fast	NH_3 slip	1.8%	3.3%	3.7%	11.2%
	SS	fast	Parasitic NH_3 oxidation	0.6%	0%	0%	0%
	SS	fast	N_2O selectivity	0.6%	0.5%	0.6%	1.2%
	SS	fast	NO_2/NO_X effluent	13.2%	10.4%	39.2%	24.9%
	D	fast	NH_3 storage (SCR)	12.1	29.7	82.1	273.9
Step 7	SS	fast	NH_3 oxidation (by O_2)	17.9%	11.9%	6.2%	5.2%
	D	fast	NH_3 storage (vacant)	186.0	221.4	391.7	322.7
Step 8	D	fast	NH_3 storage (total)	193.8	267.7	669.0	824.1

What are we looking for?

- SCR activity

  SCR activity *SHOULD* provide good indication if we are producing NO_2 insitu

  - Standard (NO only) SCR reaction conditions should yield superior results (with inclusion of fast SCR reaction)
  - Fast (equimolar NO, NO_2) SCR reaction conditions should yield inferior results (with inclusion of NO_2-only SCR reaction)